CLAIMS

What is claimed is:

1. An apparatus for sulfonating the surface of an article with a sulfonating gas to modify and treat the surface, comprising:

an enclosable container for receiving the article therein, said container being capable of being substantially air tight to contain substantially all the sulfonating gas;

a gas inlet for introducing the sulfonating gas into the enclosable container;

an on-site and on-demand sulfur-containing gas generator in communication with the enclosable container through the gas inlet, said gas generator using a chemical feed stock selected from the group consisting of raw sulfur, processed sulfur, sulfur dioxide, liquid sulfur dioxide, sulfur trioxide, sulfuric acid and mixtures thereof to produce the sulfur-containing gas at a predetermined concentration;

a source of dry air for mixing with the sulfur-containing gas to form a sulfonating gas; and

a pump for pumping the sulfonating gas into the enclosable container,

whereby some of the sulfur in the sulfonating gas is consumed to form the treatment layer on the surface of the article.

2. The apparatus of claim 1, further comprising a means for exhausting the sulfonating gas from the enclosed container after the treatment has been effected.

3. The apparatus of claim 1, further comprising a means for neutralizing the sulfonated treated surface, including a source of a neutralizing agent selected from the group consisting of ammonia, calcium, aluminum and any positively charged ion-containing fluid and solutions and mixtures thereof, and a means for removing the neutralizing agent after it has neutralized the sulfonated article.

4. The apparatus of claim 1, wherein the sulfonating gas includes sulfur trioxide and dry air.

5. The apparatus of claim 1, further comprising an in-line heater to heat the dry air for the production of hot, dry air to be combined with the sulfur-containing gas made by the gas generator to form a hot sulfonating gas mixture.

6. The apparatus of claim 2, further comprising a gas carrier from the exhaust means to the gas inlet so that the exhaust sulfonating gas may be recycled and re-used.

7. The apparatus of claim 6, wherein the recycling gas carrier is in line with the gas generator so that the sulfur content of the sulfonating gas may be rejuvenated to a concentration of a level from about 1% to about 20% by volume of the sulfonating gas.

8. The apparatus of claim 1, further comprising a sulfur-containing gas sensor for monitoring the concentration of sulfur in the sulfur-containing gas, whereby information from the sensor can be utilized to maintain a concentration of sulfur in the sulfur-containing gas to a level of between about 1% to about 20% by volume, thereby enabling recycling of the gas.

9. The apparatus of claim 1, wherein said gas generator includes a vanadium catalytic converter for the on-site production of sulfur-containing gas from a sulfur-containing compound selected from the group consisting of raw sulfur, processed sulfur, sulfur dioxide, liquid sulfur dioxide, sulfur trioxide, sulfuric acid and mixtures thereof.

10. An apparatus for sulfonating an enclosed vessel with a sulfonating gas to modify and effect a treatment on the interior surface of the vessel, comprising:

at least one inlet to be inserted into the enclosed vessel for injecting sulfonating gas into the vessel, said inlet including a means for effecting a substantially airtight seal before the gas is injected into the vessel;

a gas manifold having at least one gas carrier connected to the at least one inlet;

an on-site and on-demand sulfur-containing sulfonating gas generator in communication with the at least one inlet through the gas manifold, said gas generator utilizing a chemical feed stock selected from the group consisting of raw sulfur, processed sulfur, sulfur dioxide, liquid sulfur dioxide, sulfur trioxide, sulfuric acid and mixtures thereof to produce the sulfur-containing gas;

a source of dry air to be mixed with the sulfur-containing gas to form the sulfonating gas; and

a pump for pumping the sulfonating gas through the injection inlets into the enclosed vessel,

whereby the interior surface of the enclosed vessel has a treatment imparted thereon by consuming some of the sulfur in the sulfonating gas to form a treated layer.

11. The apparatus of claim 10, further comprising a means for exhausting the sulfonating gas from within the enclosed vessel.

12. The apparatus of claim 10, further comprising a means for neutralizing the treated interior surface of the vessel, including a means for introducing a neutralizing agent into the interior of the vessel, said neutralizing agent being selected from the group consisting of ammonia, calcium, aluminum, and any positively charged ion-containing fluid and solutions and mixtures thereof, such that the enclosed vessel has been neutralized.

13. The apparatus of claim 10, wherein said gas generator includes a vanadium catalytic converter for the on-site production of sulfur-containing gas from a sulfur-containing compound selected from the group consisting of raw sulfur, processed sulfur, sulfur dioxide, liquid sulfur dioxide, sulfur trioxide, sulfuric acid and mixtures thereof.

14. The apparatus of claim 10, further comprising a sensor for monitoring the concentration of sulfur in the sulfur-containing gas, whereby information from the sensor can be

utilized to replenish and maintain a concentration of sulfur in the sulfur-containing gas to a level of between about 1% to about 20% by volume, thereby enabling recycling of the gas.

15. The apparatus of claim 10, wherein the vessel includes vessels made of a polymeric material.

16. The apparatus of claim 10, wherein the vessel includes a plastic automotive gasoline tank.

17. The apparatus of claim 10, wherein the at least one inlet includes an injection nozzle adapted for mating with the enclosure of the enclosed vessel to effect an airtight seal.

18. An apparatus for applying a sulfonating treatment or surface modification onto the surface of polymeric articles, comprising:

a multi-port gas delivery system having individual ports for connecting to a plurality of individual polymeric articles;

a plurality of means for introducing a sulfonating gas onto the surface of individual polymeric articles such that a treatment is formed on the surface of the article, said sulfonating gas being comprised of dry air and a sulfur-containing gas, said dry air being at an elevated temperature of between about 15°C and 70°C, and said sulfur-containing gas including a mole percentage of elemental sulfur within the sulfur-containing gas of from about 1% to about 20%, said elemental sulfur being sourced from a chemical feedstock selected from the group consisting of raw sulfur, processed sulfur, sulfur dioxide, liquid sulfur dioxide, sulfur trioxide, sulfuric acid and mixtures thereof, whereby some of the sulfur in the sulfur-containing gas is consumed to form the treatment layer;

a manifold means for containing and transporting the sulfonating gas between the multiple ports of the gas delivery system so that the unused sulfonating gas can be recycled and delivered to additional polymeric articles for more of the elemental sulfur to be consumed by forming a treatment layer on more of the articles;

a means for introducing a neutralizing agent onto the surface of the polymeric articles, said neutralizing agent being selected from the group consisting of ammonia, calcium, aluminum and any positively charged ion-containing fluid and mixtures and solutions thereof; and

a vanadium catalytic converter gas generator for the on-site production of sulfur-containing gas from a sulfur-containing compound feedstock selected from the group consisting of raw sulfur, processed sulfur, sulfur dioxide, liquid sulfur dioxide, sulfur trioxide, sulfuric acid and mixtures thereof, said on-site production of the sulfur-containing gas being adapted to replenish the sulfur mole percentage concentration in the spent sulfur-containing gas to a level of between about 1% to about 20%, based upon the volume of the sulfur-containing gas being generated,

whereby an effective concentration of sulfur-containing compound is present in the sulfonating gas and may be reused and recycled for sulfonating additional articles.

19. The apparatus of claim 18, further comprising a means for exhausting the sulfonating gas from the interior of the enclosed vessel.

20. The apparatus of claim 18, wherein the at least one inlet includes substantially airtight injection nozzles.

21. The apparatus of claim 18, further comprising an in-line sensor monitor for detecting the sulfur concentration in the sulfur-containing gas to enable replenishing of the sulfur content of the sulfonating gas to bring it back to full strength.

22. A method of sulfonating an article to effect a surface treatment, comprising:

placing at least one article in an enclosable container, said container being capable of being substantially air tight, and sealing the at least one article into the container;

on-site generating of a sulfur-containing gas by a gas generator utilizing a chemical feed stock selected from the group consisting of raw sulfur, processed sulfur, sulfur dioxide, liquid sulfur dioxide, sulfur trioxide, sulfuric acid and mixtures thereof;

providing dry air from a source of dry air to be mixed with the sulfur-containing gas to form a sulfonating gas;

pumping the resultant sulfonating gas into the enclosable container until the surface treatment is effected, whereby a resulting treated article has consumed some of the sulfur in the sulfur-containing gas to form the treatment layer.

23. The method of claim 22, further comprising the step of exhausting the sulfonating gas from the enclosed vessel after sulfonation.

24. The method of claim 22, further comprising a step of neutralizing the treated surface with a neutralizing agent being selected from the group consisting of ammonia, calcium, aluminum and any positively charged ion carried by a fluid and mixtures and solutions thereof.

25. The method of claim 22, further comprising heating the dry air before mixing with the sulfur-containing gas.

26. The method of claim 22, further comprising a step of monitoring the concentration of the sulfur compound within the sulfur-containing gas after exhausting and replenishing the sulfur concentration of the exhaust gas back to a level of between about 1% and about 20% by volume, whereby the resultant replenished sulfur-containing gas may be recycled and re-used.

27. The method of claim 23, further comprising the step of on-site generating more sulfur-containing compound to be put in the sulfonating gas which has been recycled from a previous sulfonating treatment, mixing said recycled gas with heated dry air to form a replenished sulfonating gas and recycling the replenished mixture back into the enclosed container to perform more sulfonation treatment.

28. The method of claim 22, wherein the step of on-site generating of a sulfur-containing gas is accomplished by oxidizing sulfur dioxide into sulfur trioxide.

29. The method of claim 22, wherein the step of on-site generating of the sulfur-containing gas includes a two step process of first burning elemental sulfur to form sulfur dioxide followed by oxidizing the sulfur dioxide into sulfur trioxide, and then utilizing the sulfur trioxide to effect the treatment of the article surface.

30. The method of claim 22, wherein the step of on-site generating of the sulfur-containing gas is accomplished by pumping liquid sulfuric acid into a vaporizer and then mixing the air.

31. A method of sulfonating an enclosed vessel to sulfonate the interior surface of the vessel, comprising:

on-site generating of a sulfur-containing gas from a chemical feedstock selected from the group consisting of raw sulfur, processed sulfur, sulfur dioxide, liquid sulfur dioxide, sulfur trioxide, sulfuric acid and mixtures thereof;

providing dry air from a source of dry air and mixing same with the sulfur-containing gas to form a sulfonating gas;

injecting the sulfonating gas into the enclosed vessel until the surface treatment is effected, whereby a resulting treated article has consumed some of the sulfur from the sulfur-containing gas to form a sulfonated layer.

32. The method of claim 31, further comprising a step of exhausting the sulfonating gas after the sulfonation has taken effect.

33. The method of claim 32, further comprising a step of neutralizing the treated vessel by injecting a neutralizing agent selected from the group consisting of ammonia, calcium, aluminum and any positively charged ion-containing fluid, and solutions and mixtures thereof, and a means for removing the neutralizing agent after it has neutralized the sulfonated article.

34. The method of claim 31, further comprising a step of heating the dry air before mixing with the sulfur-containing gas.

35. The method of claim 31, further comprising a step of monitoring the sulfur concentration of the sulfur compound within the sulfur-containing gas after exhausting and replenishing the sulfur concentration of the exhaust gas back to a level of between about 1% and about 20% by volume, whereby the resultant replenished sulfur-containing gas may be recycled and re-used.

36. The method of claim 35, further comprising a step on on-site generating of more sulfur-containing gas to replenish the sulfur concentration to a mole percentage of between about 1% and about 20%, and utilizing that replenished gas for sulfonating the enclosed vessel.

37. The method of claim 31, wherein the step of on-site generating of a sulfur-containing gas is accomplished by generating sulfur trioxide from elemental sulfur.

38. The method of claim 31, wherein the step of on-site generating of a sulfur-containing gas is accomplished by generating sulfur trioxide from sulfur dioxide.

39. The method of claim 31, wherein the step of on-site generating of the sulfur-containing gas is accomplished by pumping liquid sulfuric acid into a vaporizer and then mixing the air.

40. The method of claim 31, wherein the enclosed vessel is made of a polymeric material.

41. The method of claim 31, wherein the enclosed vessel is an automotive plastic gasoline tank.

42. An article made by the methods and apparatuses of claims 1 through 41.

43. The article of claim 42, wherein the article includes an automotive plastic gasoline tank.